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A relatively recent addition to the large number of potentially useful high polymeric materials is allyl starch. This product is an ether derivative of starch which is usually prepared by reacting either allyl chloride or allyl bromide with a whole starch paste in the presence of a suitable catalyst. Several variations of this general procedure have been reported in the literature[1,2,3].

The product may be described as an oxidizable high polymer. It possesses substantial unsaturation through which it can react with oxygen to form an insoluble, infusible mass. In addition, it is comparatively high in molecular weight (10,000 - 50,000) so that, dissolved in a suitable organic solvent and spread as a thin layer, it dries rapidly by release of solvent. This unique combination of properties makes allyl starch most likely to be utilized as a coating material. Other possible applications include its use in laminating adhesives, rigid plastics, and in printing inks[4]. The purpose of this circular is to summarize briefly the properties of allyl starch with emphasis on its use as a coating material for interior applications.

Appearance of Crude Product

As presently prepared, allyl starch is recovered as an off-white, opaque, amorphous solid. This crude product contains from 20 to 30 percent of water and is soft and plastic at temperatures above 120° F. At temperatures approaching 32° F., the product is hard and brittle. In this state, it is easily pulverized and can be suspended in water if desired for special coating applications.

Drying

For most applications it is necessary to remove the water from the product. This may be accomplished by azeotropic distillation or by milling on cool compound rolls. The rolls are usually held at a temperature of approximately 100° F. If a small amount of the allyl starch is put on the mill, it bands readily and serves as a leader for the addition of the remainder. It is frequently necessary to add small amounts of high boiling solvent or modifier to facilitate the milling. Part of the water evaporates during the milling and the allyl starch

[1] Nichols, P. L., Jr., and Yanovsky, E., J. Am. Chem. Soc. 67, 46 (1945).

[2] Nichols, P. L., Jr., Hamilton, R. M., Smith, Lee T., and Yanovsky, E., Ind. & Eng. Chem. 37, 201 (1945).

[3] Talley, E. A., Hamilton, R. M., Schwartz, J. H., Brown, C. A., and Yanovsky, E., Mimeograph Circular AIC-140, Eastern Regional Research Laboratory (February 1947).

[4] General Mills, Inc., Chemical Engineering 54, 175, November 1947.

develops considerable toughness so that it can be stripped from the mill as a thin sheet without difficulty. With experience, the mill operator will be able to judge the optimum conditions of temperature and residual water which facilitate the removal of the material from the rolls. The milled sheet is pliable and self-supporting so that it may be suspended in the air to dry. Usually two to four hours drying at room temperature is sufficient depending upon the relative humidity of the atmosphere. When dry, the sheet is transparent, amber in color, and extremely brittle.

Azeotropic distillation and milling on cool compounding rolls have been found to be satisfactory in the laboratory. However, other methods for large-scale operation such as drum or spray drying are likely to be more efficient. If elevated temperatures are used to facilitate drying, it should be remembered that the unoxidized allyl starch has a melting point in the neighborhood of 200° F.

A method for spray drying allyl starch has been developed recently which merits attention. It consists essentially in selecting a low boiling solvent or solvent mixture for the reaction product which is relatively hydrophobic, as for example 40 parts of benzene to 60 parts of acetone. In the experiments indicated, the benzene was added to the acetone in the above proportion after the reaction was complete. However, it is anticipated that the mixed solvent can be added to the reaction mixture in place of the acetone without materially affecting the allyl starch produced. When the reaction is complete and the pH of the mixtures has been adjusted to neutrality, the mixture is transferred to a settling tank to allow the bulk of the salts to settle out. The supernatant layer containing the allyl starch is drawn off and passed through a high speed centrifugal clarifier to remove the residual water phase and insoluble material. The clarified solution may then be dried at room temperature by conventional spray drying techniques without the necessity of excluding air from the system. Spray drying is facilitated by preheating the solution to 130-140° F. shortly before it reaches the jets. The dried product is an off-white, amorphous powder which is readily dissolved in suitable solvents. A 35-percent solution of spray dried allyl starch in 50:50 toluene and n-butanol has a color of #10 on the Gardner scale, a viscosity of 0.5-1.3 poises and is briliantly clear.

The method possesses several advantages over procedures heretofore used. It eliminates the necessity for the steam distillation step normally required for the removal of the organic solvents. In addition, the subsequent water washing step to remove water soluble constituents, e.g. salts, and starch fractions of low substitution is no longer required. Furthermore, the centrifugal clarification step prior to spray drying makes it unnecessary to clarify the prepared lacquer.

solvents. This behavior emphasizes the necessity for controlling cure if solvent resistance is to be properly evaluated.

The incorporation of moderate amounts of compatible, non-drying resin modifiers does not appear to materially improve the water resistance of cured coatings using allyl starch having the stated substitution. However, work in this direction has been of a preliminary character, and further study is indicated.

It is convenient at this point to mention certain other properties of allyl starch coatings which bear upon the workability of the material. In multiple coat application, difficulty may be encountered in obtaining adhesion to an undercoat if the undercoat has been allowed to harden. Best results are obtained when each coat is applied as soon as the working characteristics of the material will permit. For example, multiple spray coats of the clear lacquer, each having a dry thickness of .001 inch may be applied on a 1/2 hour schedule. For brush application, the interval between coats must be increased to prevent excessive re-dissolving of the undercoat. The presence of large amounts of butanol in the recipe is likely to cause lifting of the undercoat.

Modifiers

It was indicated in the foregoing paragraphs that allyl starch of the stated substitution requires the addition of a plasticizer to relieve the stress which develops in the coating upon the release of solvent. Compatible resin modifiers appear to be particularly beneficial for this purpose. A representative list of modifiers which have been examined for compatibility with allyl starch of the stated substitution is given in Table I[7]. The table includes at least two modifiers having borderline compatibility and several abietic acid derivatives which are compatible but retard the cures even when used in as little as one part modifier to 100 parts of allyl starch. These abietic acid derivatives are possibly useful as anti-gelling agents for allyl starch lacquers.

Combinations of hard and soft non-reactive resin modifiers may be used advantageously in large proportions to supplement the properties of allyl starch in baking enamels. An example of this type of formulation is given in Table IV.

Pigments

Because of the generally poor weathering resistance of clear allyl starch lacquers, the investigation of pigmented systems for exterior use has been limited. However, certain conclusions may be drawn from the exploratory work which has been completed.

White enamels have been prepared from allyl starch using titanium dioxide as the pigment. Usually the pigment is pebble-milled for 24 hours

[7] THE MENTION OF COMMERCIAL PRODUCTS DOES NOT IMPLY THAT THEY ARE ENDORSED OR RECOMMENDED BY THE DEPARTMENT OF AGRICULTURE OVER OTHERS OF A SIMILAR NATURE NOT MENTIONED.

with a portion of the allyl starch vehicle. No difficulty is likely to be encountered in wetting the pigment and obtaining a fine dispersion. An enamel consisting of 2 parts of pigment to 3 parts of binder (6.4 parts of vehicle) levels well and dries, free from tack, in 15 minutes. It may be used as a baking enamel if it is to be applied on a rigid surface where a high degree of abrasion resistance is desired. The enamel exhibits good gloss and color retention when cured at temperatures up to 350° F. This enamel may also be used in air drying applications provided a suitable catalyst is added. Coatings containing catalyst which are exposed to the air at room temperature become abrasion resistant in from 24 to 48 hours.

TABLE I

Compatibility of Modifiers with Allyl Starch (1.8 substitution) for the Allyl Starch-Modifier Ratios of 10:1 and 5:5

Modifier	Compatibility 10:1	1:1	Modifier	Compatibility 10:1	1:1
Bakelite BR 13260[a]	C	-	Paraplex AL 111[h]	I	-
Bakelite BR 13202[a]	-	I	Paraplex RG 2[h]	Q	I
Bakelite BR 256[a]	C*	-	Paraplex RG 7[h]	C	-
Bakelite XJ 10433[a]	-	I	Paraplex G 25[h]	I	I
Limed Rosin	C*	-	Duraplex ND 75[h]	C	C
Abalyn[b]	C*	-	Aroclor 1242[i]	C	-
Vinsol[b]	C*	-	Aroclor 1260[i]	C	-
Pentacizer 81[c]	C	-	Aroclor 4465[i]	-	I
Pentacizer 131[c]	C	-	Linseed oil, aged raw[j]	I	-
Glyptal 1202[d]	I	-	Linseed oil, Minnesota 2B[j]	I	-
Glyptal 1276[d]	C	-	Linseed oil, blown[j]	I	-
Esterol 4651[e]	C	C	Beckosol, solid #24[k]	I	-
Plasticizer 173-16[f]	C	C	Beckosol 1323[k]	Q	-
Cumar Resin V-2[g]	C	I	Beckosol 1308[k]	C	Q
Beeswax	I	-			

Key: C - compatible, I - incompatible, Q - questionable
* - retards cure of allyl starch

a Bakelite Corporation, Bloomfield, N. J.
b Hercules Powder Company, Wilmington, Delaware
c Heyden Chemical Corporation, Garfield, N. J.
d General Electric Company, Schenectady, N. Y.
e Paramet Chemical Corporation, Long Island City, N. Y.
f Pittsburgh Plate Glass Co., Milwaukee, Wisconsin
g Barrett Division, Allied Chemical & Dye Corporation, New York, N. Y.
h Resinous Products & Chemical Corp., Philadelphia, Pa.
i Monsanto Chemical Company, St. Louis, Mo.
j Minnesota Linseed Oil Paint Co., Minneapolis, Minn.
k Reichold Chemicals Inc., Elizabeth, N. J.

Stability of the Dehydrated Product

Generally, the dried allyl starch flakes may be stored in a sealed can for periods up to one week at room temperature without becoming insoluble, provided the can is completely filled. However, it is preferable to dissolve the material in a suitable solvent as soon as convenient after drying. Although a sample of allyl starch may still be soluble following prolonged exposure to the atmosphere, sufficient oxidative changes are likely to have occurred to adversely affect the storage stability of the prepared lacquer or paint.

Solubility Characteristics

In allyl starch of the type discussed herein, the mean degree of substitution is fixed at about 1.8 allyl groups per glucose unit leaving a calculated residual hydroxyl content of 1.2 groups. It is these hydroxyl groups which influence so strongly the solubility and viscosity characteristics of the product. Allyl starch having this degree of substitution is soluble in most alcohols, esters, ketones, and some ethers. It is almost completely soluble in benzene, and partially soluble in toluene or xylene but is insoluble in aliphatic hydrocarbons. It is readily soluble in mixtures of an aromatic hydrocarbon and a polar solvent, as for example an 80:20 mixture of xylene-butanol or toluene-ethanol. Unless large amounts of suitable polar solvents are present, the tolerance of allyl starch for petroleum thinners is very limited.

Properties of Solutions

It is usually desirable to introduce a clarification step in the preparation of allyl starch solutions to remove the small amount of insoluble matter which may be present. A filtered solution is light amber in color and brilliantly clear.

A solution of 40 percent non-volatile in an efficient solvent mixture has a viscosity of approximately 1.0 poise. Because of its low intrinsic viscosity, allyl starch may be formulated to yield lacquers of exceptionally high solids content. At both brushing and spraying viscosities, the solution exhibits good body and when applied as a brush or spray coat over an impervious surface, the solution levels well with no tendency to sag or wrinkle. When applied over a material such as filled oak or mahogany, for example, the filler has been observed to cause creeping of the wet coating. This effect is probably more marked in allyl starch than in most commercial coating materials because of its relatively high polarity which makes it particularly dependent on the maintenance of balance between polar and non-polar components in the solvent mixture.

Brush or spray coatings of nominal thickness dry, free from tack, in from 5 minutes to 20 minutes depending upon the volatility of the solvents used.

Properties of Dry Coatings

Following one-half to one hour air drying, a coating of allyl starch is both print and block resistant but not scratch or mar resistant. Abrasion resistance develops later as a result of oxidative hardening.

The coating is heat reactive so that it may be baked at elevated temperatures to acquire the desired hardness. The time required to effect maximum cure as measured by resistance to spotting with a solution of malachite green in equal parts of acetone and acetic acid, is roughly 4 hours at 100° C. or 15 minutes at 150° C. Maximum abrasion resistance is developed within the curing times indicated.

The coating is also capable of hardening at room temperature particularly if a suitable oxidation catalyst is employed. Cobalt napthenate (0.075 percent by weight of Co based on total resin weight) has been used most generally for this purpose. An allyl starch coating containing the necessary drier acquires serviceable scratch or mar resistance in from 24 to 48 hours at room temperature.

When an unmodified allyl starch coating is air-dried, it develops a fine pattern of cracks. This cracking is first observed in from 2 to 8 hours after the coating is applied, and is interpreted as the result of excessive shrinkage of the coating accompanying the release of solvent. The addition of as little as ten parts of a monomeric plasticizer such as tricresyl phosphate or dibutyl phthalate per 100 parts of allyl starch prevents the coating from cracking. Polymeric plasticizers appear to be equally effective for this purpose and, in addition, their use permits the formulator to control the hardness of the coating. For example, up to 50 parts or more of a modifying resin such as a non-drying alkyd may be added to 100 parts of allyl starch without materially altering the drying properties or curing characteristics of the product.

Cured, unmodified allyl starch coatings possess the low distensibility which is characteristic of thermosetting materials. Similarly, cured coatings of allyl starch, modified with a non-drying alkyd, for example, exhibit improved distensibility to the extent that they are able to pass the test of bending over a 1/8 inch mandrel[5]. However, these same coatings of modified allyl starch usually do not have sufficient distensibility to "ribbon" when tested with the point of a knife[6].

Cured coatings of unmodified allyl starch possess exceptional resistance to most organic solvents including alcohols, esters, ethers, and ketones, as well as aromatic, chlorinated, and aliphatic hydrocarbons. However, they have poor resistance to water and aqueous solutions such as 50 percent ethanol, 5 percent sodium hydroxide, 10 percent ammonium hydroxide and 5 percent phenol. Incompletely cured coatings are resistant to boiling water and dilute alkali, but are swollen by polar

[5] D 522-41 of ASTM

[6] Federal Specification TT-P-141a, Method 617

Suggested Formulations

The following formulations are presented to assist the investigator in evaluating the product. They do not necessarily represent the best combination of ingredients but have been found to give promising results in the laboratory.

Generally speaking, the purpose of the modifying resin is to improve flexibility, water resistance, and adhesion of the allyl starch. The amount of modifying resin, ten parts or more, which may be added is limited by the fact that excessive amounts tend to inhibit cure. However, it is possible to use up to 140 parts of modifying resins per 100 parts of allyl starch in baked coatings if desired. Suggested formulations for allyl starch coatings are given in Tables II, III, and IV.

TABLE II

Clear Wood Lacquer for Brush Application

Allyl starch	100
Non-oxidizing resin*	50
Ethanol	10
Butanol	10
Butyl Cellosolve	20
Xylene	130
Cobalt napthenate (6%) (0.075% Co based on total resin)	1.87

*as, for example, Beckosol #1308, Aroclor 1242, Duraplex ND 75, Plasticizer 173-16, or Esterol 4651

TABLE III

Clear Spraying Lacquer

Allyl starch	100
Non-oxidizing resin*	50
Ethanol	4
Ethyl acetate	12
n-Butanol	22
Butyl acetate	67
Toluene	45
Cobalt napthenate (6%) (0.075% Co based on total resin)	1.87

*as, for example, Beckosol #1308, Aroclor 1242, Duraplex ND 75, Plasticizer 173-16, or Esterol 4651

TABLE IV

White Baking Enamel for Spray Application

	Parts by weight
Paste:	
Titanium dioxide, rutile	26
Paraplex RG-7 (60% in xylol)	21.5
xylene	14.5
n-butanol	9.5
Mix with:	
Allyl Starch[a]	13
toluene	14
ethanol	1.5
	100.0

Total Solids	51.9 %
Pigment	50. %
Binder	50. %
Viscosity	0.5 poise
Curing Time	20 min. at 300° F.
Thinner	toluene

(a) dissolve dry allyl starch in toluene and ethanol and clarify

Discussion

In considering the properties of allyl starch, it must be kept in mind that the product, as presently prepared, is a heterodisperse polymer of non-uniform substitution. During the etherification procedure, allyl starch undergoes substantial degradation, and the fragments of low molecular weight which are formed presumably affect the physical properties of the dry coating. It has also been found that there is considerable spread in the degree of substitution of various fractions of allyl starch. For a sample which has a mean substitution of 1.8 allyl groups, the spread in degree of substitution of various fractions is likely to be from 1.35 to 1.95. The presence of these highly polar fractions of low substitution adversely affect both the solvent resistance of the coating and the compatability of the material with various modifiers.

Because of the inhomogeneous nature of the product, it is to be expected that variations in properties will result from variations in method of production.